

<b>REPORT DOCUMENTATION PAGE</b>			Form Approved OMB NO. 0704-0188		
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) 28-04-2015		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 1-Feb-2014 - 31-Jan-2015	
4. TITLE AND SUBTITLE Final Report: Functional Nanomaterial's Synthesis and Characterization			5a. CONTRACT NUMBER W911NF-14-1-0036		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 206022		
6. AUTHORS Subramanian Ramakrishnan			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES Florida A&M University 1700 Lee Hall Drive 400 Foote-Hilyer Admin Center Tallahassee, FL 32307 -6600			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 64706-MS-REP.1		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT The aim of this proposal is to purchase equipment at Florida A&M University (FAMU) which will play a key role in synthesis and characterization of nanoparticles and polymers. Current progress is being made at Argonne National Labs (ANL) and at AFRL in characterization methods but the goal is to use the equipment at FAMU year round to carry forward the research and to provide a continuous education tool to minority students. The requested equipment will play an important role in synthesizing and characterizing the functional materials of interest to DOD and will help understand the link between material properties to polymer and particle properties at FAMU. The					
15. SUBJECT TERMS light scattering, rheology, HPLC, Diffusing Wave Spectroscopy					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			Subramanian Ramakrishnan
					19b. TELEPHONE NUMBER 850-410-6159



## Report Title

Final Report: Functional Nanomaterial's Synthesis and Characterization

### ABSTRACT

The aim of this proposal is to purchase equipment at Florida A&M University (FAMU) which will play a key role in synthesis and characterization of nanoparticles and polymers. Current progress is being made at Argonne National Labs (ANL) and at AFRL in characterization methods but the goal is to use the equipment at FAMU year round to carry forward the research and to provide a continuous education tool to minority students. The requested equipment will play an important role in synthesizing and characterizing the functional materials of interest to DOD and will help understand the link between material properties to polymer and particle properties at FAMU. The research program will educate and introduce FAMU students to modern instrumentation and help answer state of the art questions in materials characterization and processing.

---

**Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:**

**(a) Papers published in peer-reviewed journals (N/A for none)**

Received

Paper

**TOTAL:**

**Number of Papers published in peer-reviewed journals:**

---

**(b) Papers published in non-peer-reviewed journals (N/A for none)**

Received

Paper

**TOTAL:**

**Number of Papers published in non peer-reviewed journals:**

---

**(c) Presentations**

Number of Presentations: 0.00

---

**Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

Received      Paper

**TOTAL:**

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

---

**Peer-Reviewed Conference Proceeding publications (other than abstracts):**

Received      Paper

**TOTAL:**

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

---

**(d) Manuscripts**

Received      Paper

**TOTAL:**

Number of Manuscripts:

Books

Received      Book

TOTAL:

Received      Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Faheem Muhammed	0.00	
Divya Bahadur	0.00	
Onyeka Oparaji	0.00	
Emily Hammel	0.00	
Parth Vakil	0.00	
Jolie Frketic	0.00	
FTE Equivalent:	0.00	
Total Number:	6	

### Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Golda C Louis	0.00
<b>FTE Equivalent:</b>	<b>0.00</b>
<b>Total Number:</b>	<b>1</b>

### Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Subramanian Ramakrishnan	0.00	
Daniel Hallinan	0.00	
Geoffrey Strouse	0.00	
Anant Paravastu	0.00	
Tarik Dickens	0.00	
<b>FTE Equivalent:</b>	<b>0.00</b>	
<b>Total Number:</b>	<b>5</b>	

### Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Jason Madinya	0.00	
Herbert Washington	0.00	
Jhanelle Brown	0.00	
Crystal Lipscomb	0.00	
Damon Williams	0.00	
Zachary Noonon	0.00	
<b>FTE Equivalent:</b>	<b>0.00</b>	
<b>Total Number:</b>	<b>6</b>	

### Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: ..... 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

### Names of Personnel receiving masters degrees

<u>NAME</u>
<b>Total Number:</b>

**Names of personnel receiving PhDs**

NAME

**Total Number:**

**Names of other research staff**

NAME

PERCENT SUPPORTED

**FTE Equivalent:**

**Total Number:**

**Sub Contractors (DD882)**

**Inventions (DD882)**

**Scientific Progress**

"See Attachment"

**Technology Transfer**

## **Final Report**

Proposal Number: 64706-MS-REP

Agreement Number: W911NF-14-1-0036

### **Title: Functional Nanomaterial's Synthesis and Characterization**

**Subramanian Ramakrishnan**

Associate Professor, Department of Chemical and Biomedical Engineering

FAMU-FSU College of Engineering

sramakrishnan@fsu.edu

The aim of this proposal is to purchase equipment at Florida A&M University (FAMU) which will play a key role in synthesis and characterization of nanoparticles and polymers. The proposed project is the first of its kind in the college of engineering at FAMU to produce novel materials and **to integrate the research with the national high magnet field laboratory (NHMFL) in Tallahassee**. NHMFL is a state of the art national user facility right next to FAMU. This is an important development which will help in developing research capabilities of FAMU faculty and an excellent education opportunity for FAMU students. This will also sow the seed for future proposals to a number of agencies.

***S. Ramakrishnan has been allotted lab space in NHFML.*** This has directly resulted from the DOD equipment grant and the DOD research grant. All of the purchased equipment is in NHMFL. As a result of this for the first time a memorandum of understanding is being signed between FAMU and NHFML. This key development will play an important role in furthering the research capabilities of FAMU faculty and educating minority students.

All equipment has been purchased and has been installed in the laboratory. The purchased equipment include

**Equipment 1** (Eq1): Chromatography with light scattering detectors for characterization of material properties (size, molecular weight, size and molecular weight distribution, branching in polymers and charge).

**Equipment 2** (Eq2): An NMR probe to study dynamics and structure of polymers, peptides and particles.

**Equipment 3** (Eq3): Diffusing Wave Spectroscopy (DWS) to study the dynamics of particles and peptides

**Equipment 4** (Eq4): Polymer Melt Rheology and Magneto Rheology Setup: to study the rheological properties of particle gels and polymer particle composites.

The projects that the equipment is being used for is given below followed by the list of students it has impacted (graduate and undergraduate) and the collaborations it has promoted.

**1) Structure and Dynamics of Polymer Grafted Silica Nanoparticles:** This is a department of defense grant which involves the synthesis and characterization of polymers and grafting silica particles with polymers of different molecular weights and graft densities. Forming composites from just particles to which polymers are grafted (without any added matrix polymer) helps control the structure of the composite and avoids issues of agglomeration when a matrix polymer is present. The aim is to understand structure-function relationships in these nanoparticles for use in defense applications.

Eq1 is playing a key role in characterizing the synthesized polymers – molecular weight, polydispersity, intrinsic viscosity.

Eq2 will help us characterize the conformation of polymers at the particle interface and in characterizing polymer dynamics.

Eq3 will help us characterize the particle dynamics in the composite.

Eq4 will help us in measuring the rheological properties of the composite.

**Personnel:** Subramanian Ramakrishnan (PI), Golda Chakkalakal Louis (Post-doctoral associate), Jhanelle Brown (FAMU junior undergraduate student), Crystal Lipscomb (FAMU, honors thesis student), Jason Madinya (junior undergraduate student – recipient of a \$4000 summer 2015 research award for work on using DWS to characterize particle dynamics).

Experiments at NHMFL will be coupled with experiments at the Advanced Photon Source at Argonne National Labs to connect particle structure and dynamics to macroscopic properties.

**2) Polymer Nanoparticle Composites for Positive Electrodes of Lithium Batteries:** Dr. Hallinan's laboratory is controlling the chemistry at the interface between the nanoparticle electrode and the polymer electrolyte to stabilize the system at high voltages. Tuning the interaction energy between the two will also lead to a self-assembled structure that provides both high energy and high power. Controlling battery electrode stability and structure is important for developing next-generation batteries that operate at higher voltage, have higher energy density, and are more affordable. Some examples include lithium-mixed metal oxide batteries and lithium-air batteries. Homopolymers and block copolymers of different chemistries and molecular weights are being synthesized which will be characterized using the chromatography and light scattering setup.

Eq1 is being used to characterize the synthesized homo and block copolymers – molecular weight, polydispersity, charge.

Eq 4 is being used to characterize the rheological properties of the membranes and the composite.

**Personnel:** Daniel Hallinan (PI, chemical engineering), Onyeka Oparaji (graduate student), Zachary Noonon (undergraduate student).

**3) Structure and mechanical properties of peptides:** Research in Dr. Paravastu's lab centers on understanding the structure of peptides and proteins as related to diseases. Aggregation of proteins is linked to a number of diseases, including Alzheimer's, Parkinson's, and type II diabetes, but it is not clear exactly how protein self-assembly leads to pathology. The most abundant and stable components of disease-associated plaques are amyloid fibrils, which are long nanofibers composed mostly of  $\beta$ -sheets. Recent research on amyloid fibril structure has revealed the presence of multiple distinct yet energetically similar pathways to amyloid formation, and the possibility for a critical pathological role of transient low molecular weight oligomers of protein molecules. We are investigating the mechanisms of aggregation of the Alzheimer's  $\beta$ -amyloid peptide (Ab) using methods from colloid and polymer science, including light scattering, Quartz Crystal Microbalance (QCM), and rheology. Information on transient processes in protein self-assembly will be complemented by structural characterization of stable aggregates by electron microscopy and solid state NMR.

Eq1 is being used to characterize the molecular weight of synthesized peptides and to detect the formation of aggregates (dimers, oligomers etc.)

Eq2 is being used to characterize the structure of the formed fibrils from the peptides.

Eq3 will be used to characterize the dynamics of peptides and to characterize the viscoelastic properties (microrheology).

**Personnel:** Anant Paravastu (PI, chemical engineering), Ben Hudson (graduate student), Danting Huang (graduate student), Damon Williams (NHMFL research experience for undergraduates summer 2015 award recipient).

**4) Magnetic Nanocomposites for NASA:** The two main research themes in this work deal with *developing magnetic composites* for permanent magnets and novel multifunctional materials with electronic, magnetic and radiation *shielding properties*. The proposed work **(i)** Develops new synthetic methods to prepare hard / soft composite magnets via nano-processing, **(ii)** Develops characterization tools to measure the microstructure and macroscopic properties with an aim of optimizing them, and **(iii)** Uses additive printing technologies in the fabrication of these components. Through the collaborations strengthened by the proposed internships with KSC, the composites will be integrated into aerogel and self-healing composite materials

Eq1 is being used to characterize the nanoparticles and polymers synthesized in the work.

Eq2 is planned to be used for characterizing the conformation of polymers next to the magnetic nanoparticles.

Eq4 is being used to characterize the magneto-rheological properties of the synthesized composites.

**Personnel:** Subramanian Ramakrishnan and Tarik Dickens (faculty PI's, industrial engineering), Faheem Muhammed (graduate student, NASA fellow), Jolie Frketic (graduate student), Herbert Washington (undergraduate student)

**5) Nanomaterials for solid state lighting and energy efficiency:** Research in Dr. Strouse group centers on synthesizing nanomaterials (quantum dots) for solid state lighting, spin electronics and magnetic composites for advanced motor technology to reduce size, power demands and to improve performance.

Eq1 is being to characterize the novel nanoparticles synthesized – size, charge, shape.

Eq3 is planned to be used to characterize particle dynamics

Eq4 will be used to characterize the rheological properties once a composite is formed.

**Personnel:** Geoffrey Strouse (PI, chemistry), Parth Vakil (graduate student).

**Collaborations:** As can be seen from the projects listed above the equipment has involved a number of investigators from across the campus to work on interesting problems. Dr. Ramakrishnan is an expert in characterization of particles and polymers, Dr. Paravastu is an expert in solid state NMR characterization of materials, Dr. Hallinan is an expert in polymer synthesis and characterization for battery applications, Dr. Dickens is an expert in processing and additive printing of materials and Dr. Strouse is an expert in the synthesis of quantum dots and magnetic nanomaterials. As can be seen the techniques of the different investigators are complimentary and this has already resulted in different people working together.

In project 1, Dr. Ramakrishnan is being helped by Dr. Paravastu in making solid state NMR measurements to study polymers at interfaces. This has resulted in Dr. Ramakrishnan helping Dr. Paravastu characterize his peptides using light scattering and rheology and thus help him get introduced to a new area of protein aggregation.

In project 2, Dr. Ramakrishnan is assisting Dr Hallinan characterize the polymers using light scattering and both of them are working together to characterize synthesized materials using X-ray scattering at Argonne National Labs. Dr. Hallinan is also working with other scientists at the magnet lab to use magnetic resonance imaging to characterize his battery materials.

In projects 4 and 5, Dr. Dickens, Dr. Strouse and Dr. Ramakrishnan have started collaborating and even submitted a center proposal to NASA.

1. S. Ramakrishnan (PI), T. Siegrist, G. Strouse and T. Dickens (August 2015 – July 2020).  
NASA - *Magnetic Nanocomposites for Aerospace Applications*, **\$5,000,000**.

The purchased equipment is playing a key part in the proposal.

In addition to the experimental researchers mentioned above, collaborations have also been established with theoretical scientists.

Dr. Ramakrishnan is working with Dr. Shanbhag in the Department of Computational Science on modeling structure and rheology of polymer nanocomposites (project 1).

Dr. Strouse and Dr. Ramakrishnan are working with Dr. Mochena (physics) who is theorist on modeling of self-assembly of quantum dots and magnetic nanomaterials. Utilizing the equipment purchased, we have recently submitted a center proposal to National Science Foundation (NSF)

1. Mochena, M. (PI), Ramakrishnan, S., Strouse, G. & Mateeva, N. (August 2015- July 2020). *NSF PREM, Magnetic Interrogation of Mesoscale Materials*, \$4,000,000.

In addition to the proposed research, the equipment is playing a key role in the education of graduate and undergraduate students working with different professors – the names of these students are mentioned in the different projects.

A lab/theory course is also being planned for the first time at FAMU and NHMFL – Nanoparticle Synthesis and Characterization by S. Ramakrishnan and the purchased equipment will play a key role in the course.